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Catalytic nitroxidation of 1-methylnaphthalene
I. Preparation, characterisation and NO-surface interactions of chromia/alumina-based catalysts

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Abstract

In view of their use in the nitroxidation of 1-methylnaphthalene into 1-naphthonitrile, chromia/alumina and K-containing chromia/alumina catalysts were prepared. They were characterised by X-ray diffraction, scanning electron microscopy, nitrogen physical adsorption, UV–vis diffuse reflectance spectroscopy, adsorption microcalorimetry of ammonia and carbon dioxide, temperature-programmed reduction. The interaction of NO with the catalyst surface was investigated by temperature-programmed methods. Both Cr(III) and Cr(VI) species were found on the catalysts, the content of the latter increasing along with the K loading. A bichromate phase was detected in the K-containing catalysts. Cr(VI) species underwent (incomplete) reduction under hydrogen atmosphere. The reduction extent was higher at the higher K loadings, though higher energy barriers needed to be overcome for its occurrence. All the catalysts were able to dissociate NO into atomic nitrogen and oxygen and also to convert NO into N_2O and O_2 in the temperature range 623–657 K. NO disproportionation occurred on the K-containing chromia/alumina catalysts even at relatively low temperatures (372–407 K), but not on chromia/alumina. Chromia/alumina showed an acidic as well as a basic character, the acid features being however predominant. At the lowest K content acidity appeared remarkably lowered and basicity significantly increased. Further addition of K originated a catalyst somewhat balanced in its (weak) acid–base character. At the highest K loadings the original acidic and basic features of chromia/alumina were completely lost. Such different redox and acid–base features, as well as the different interaction modes with NO, are expected to influence deeply the catalytic behaviour in 1-methylnaphthalene nitroxidation.

Keywords: Nitroxidation; 1-Methylnaphthalene; Chromia/alumina; TPR; Microcalorimetry

1. Introduction

The physical–chemical properties of chromia/alumina have been under intense scrutiny since the early 1960s [1], due to the industrial relevance of its uses as a catalyst. Among the possible applications of chromia/alumina catalysts, the nitroxidation of hydrocarbons, i.e. their one-step transformation into the corresponding nitriles by reaction with NO, has attracted attention [2–4]. Due to its particular features, nitroxidation could represent an interesting alternative to the ammoxidation reaction. Simpler catalyst formulation, safer operation and lower environmental impact act as driving forces for developing nitroxidation catalysts. Besides chromia/alumina, NiO- and PbO-based systems have also been indicated as promising candidates [2,3,5,6]. Concerning the reactant hydrocarbons, the focus has mostly been on propene [2,3,5], isobutene [2,3] and toluene [2–4,6]; propane, isobutane and xilenes have also been investigated in some detail [2,3]. Mostly relying on kinetic results [3–6], a redox mechanism has been proposed. Depending on the aliphatic or aromatic nature of the reactant hydrocarbon, an allylic or benzylic species would form on the surface of the oxidised catalyst. After loosing two more hydrogen atoms, this species would undergo attack by the atomic nitrogen originated through the dissociative adsorption of NO, while the atomic oxygen would re-oxidize the catalyst surface. The occurrence of parasite degradation of the reactant hydrocarbon has been tentatively ascribed

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to O_2 formed from NO disproportionation into N_2O and oxygen [5]. The acidic features of the solid would also play some role, as indicated by changes in the catalyst performance when basic MgO was included in the formulation of chromia/alumina, nikel oxide/alumina and nikel oxide/silica [3]. To the best of the present authors' knowledge, just one patent [7] reports about the nitroxidation activity of alumina-supported alkali-metal oxides and no papers dealing with alkali-metal doped nitroxidation catalysts have been published so far in the open literature. Nor did studies on the reactivity of alkylpolynuclear aromatic hydrocarbons with NO appear. Doping by alkali-metal compounds is worthy of investigation. Besides modification in the catalyst acidity, perturbation of the oxidation state of the active species involved in the redox mechanism might occur as well, both these factors being expected to influence the nitroxidation activity. The use of alkylpolyaromatics as reactants for nitroxidation deserves attention. 1-Naphthonitrile, the target product of 1-methylnaphthalene (1-MN) nitroxidation, can be easily converted into 1-naphthylamide, one of the starting compounds for the production of 2-(1′-naphthyl)-5-phenyloxazole, used as a laser dye [8]. Furthermore, the understanding of 1-MN nitroxidation might be used as a reference for the conversion of 2,6-dimethylnaphthalene into the corresponding dinitrile, from which 2,6-diaminonaphthalene can be obtained. The latter is a key product for the manufacture, by reaction with adipic acid, of polymers of superior technological properties.

The present work is a part of a series devoted to the preparation, thorough characterisation and catalytic investigation of chromia/alumina, NiO-silica and NiO-alumina for the nitroxidation of 1-methylnaphthalene, for which all these oxide systems were found to be active, though to a different extent. Results concerning the preparation and characterisation of chromia/alumina catalysts are reported here. In forthcoming papers the preparation and characterisation of NiO/silica and NiO/alumina, as well as the catalytic behaviour of both chromia- and NiO-based systems, will be dealt with.

Chromia/alumina and potassium-containing chromia/alumina catalysts were prepared by the impregnation technique. The catalysts were characterised as to their chemical composition, structure, morphology and texture by atomic adsorption (AA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and nitrogen physical adsorption–desorption, respectively. Information about the oxidation state of chromium was obtained by UV–vis diffuse reflectance spectroscopy (DRS). The redox features of the catalysts and the interaction of NO with the surface were investigated by temperature-programmed methods. Temperature-programmed reduction (TPR) was carried out under hydrogen flow. The nature of the species originating upon exposure of the catalyst surface to NO under temperature-programmed conditions was monitored by on-line mass-spectroscopy. Adsorption microcalorimetry, a direct and reliable quantitative technique for determining the extent and energy of adsorbate–adsorbent interactions, was used to investigate the surface acidity and basicity of the catalysts. Ammonia and carbon dioxide were chosen as probe molecules for assessing the concentration and strength-distribution of the acid and base sites, respectively.

2. Experimental

2.1. Catalyst preparation

The following catalysts were prepared: ACr10, nominally containing 10 wt.% of chromium on γ-alumina; ACr10K1, ACr10K2, ACr10K4 and ACr10K8, nominally containing also 1, 2, 4 and 8 wt.% of potassium, respectively. γ-Alumina (grain size 100–500 μm, surface area 121 $m^2 g^{-1}$, kindly provided by Süd Chemie MT, Novara, Italy) was obtained by calcination in air of pseudoboehmite Versal 250 La Roche at 1223 K for 4 h. The support was impregnated with comparable volumes of aqueous solutions of the appropriate amounts of CrO_3 (and $K_2Cr_2O_7$ for the ACr10KX samples). The carefully stirred paste was dried overnight at 383 K and finally calcined at 973 K for 12 h. For comparison purposes a sample of crystalline chromia was prepared as in [9]. All chemicals were Carlo Erba reagent grade.

2.2. Catalyst characterisation

Chemical analysis of the total chromium content was carried out by atomic absorption (AA, Varian SpecrAA-30) on samples previously dissolved by fusion with a mixture of KNO_3 and Na_2CO_3 (1:1 by weight). A different portion of the catalyst was repeatedly treated with 1 M NaOH solution heated to incipient boiling in order to extract Cr(VI) species, and the liquid analysed by AA. The residue was then dissolved by fusion with the mixture of KNO_3 and Na_2CO_3 and analysed by AA for determining Cr(III). The potassium content was determined by AA on fresh portions of the samples after extraction with distilled hot water.

Diffuse reflectance spectra were taken in the wavelength range 200–800 nm (50,000–12,500 cm^{-1}) with a Varian CARY 5E spectrometer equipped with a PC for data acquisition and analysis and using PTFE as a reference.

Phase analysis was performed by XRD using a Philips PW 1729 diffractometer equipped with a PC for data acquisition and analysis (software APD-Philips). Scans were taken with a 2θ step of 0.01°, using Ni-filtered Cu Kα radiation. When possible, the crystallite average size was calculated by means of the Warren and Scherrer formulae [10].

Textural analyses were carried out on a Sorptomatic 1990 System (Fisons Instruments), by determining the nitrogen adsorption/desorption isotherms at 77 K. Before analysis, the samples were heated overnight under vacuum up to 473 K (heating rate = 1 K min^{-1}).

Scanning electron microscopy (SEM) images with elemental mapping of powder samples mounted on an aluminum holder were obtained on a FEI Quanta 200 microscope equipped with an EDX analyser. Semiquantitative analysis was carried out at 29 kV by using the EDAX software applying the Z.A.F. correction procedure.

TPR profiles were obtained on a TPD/R/O 1100 apparatus (ThermoQuest), under the following conditions: sample weight 0.04 g, heating rate (from 313 to 1173 K) 20 K min^{-1}, flow rate 30 $cm^3 min^{-1}$, H_2 5% by volume in N_2; the hydrogen consumption was monitored by a thermal conductivity detector (TCD).